OPIC
OFFICE DE LA PROPRIÉTÉ INTELLECTUELLE DU CANADA

CIPO
CANADIAN INTELLECTUAL PROPERTY OFFICE

Ottawa Hull K1A 0C9

(21) (A1) 2,144,467
(22) 1995/03/13
(43) 1995/09/18

(51) Int.Cl.[6] C08L 75/00; C08J 9/12

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for the Production of Rigid Foams Containing Urethane, Urea and Biuret Groups and the Use Thereof

(72) Scholl, Hans-Joachim - Germany (Federal Republic of) ;
Heinemann, Torsten - Germany (Federal Republic of) ;
Welte, Rainer - Germany (Federal Republic of) ;

(71) Bayer Aktiengesellschaft - Germany (Federal Republic of) ;

(30) (DE) P 4409041.2 1994/03/17
(DE) P 4418993.1 1994/05/31

(57) 9 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.

PROCESS FOR THE PRODUCTION OF RIGID FOAMS CONTAINING URETHANE, UREA AND BIURET GROUPS AND THE USE THEREOF

ABSTRACT OF THE DISCLOSURE

The present invention relates to substantially closed-cell rigid foams containing urethane, urea and biuret groups and exhibiting excellent adhesion to solid surfaces, and to a process for the production of these foams. This process comprises reacting

a) a organic polyisocyanate, with
b) modified castor oil, in the presence of
c) catalysts and
d) water.

Suitable components for the modified castor oil used herein are the reaction products of castor oil with one or more amine and/or hydroxy compounds. These modified castor oil compositions have an OH number of 200 to 500, preferably 350 to 480. The invention relates also to insulating materials and/or mechanical structural components made from these foams.

PROCESS FOR THE PRODUCTION OF RIGID FOAMS CONTAINING URETHANE, UREA AND BIURET GROUPS AND THE USE THEREOF

BACKGROUND OF THE INVENTION

This invention relates to a novel process for the production of substantially closed-cell rigid foams containing urethane, urea and biuret groups. These foams have excellent adhesion to solid surfaces. This invention is also related to the use of these foams as insulating materials and/or for strengthening mechanical structural components.

Processes for the production of substantially closed-cell rigid foams containing urethane, urea and biuret groups are generally known. A review of the production of such rigid foams may, for example, be found in *Kunststoff-Handbuch*, volume VII, *Polyurethane*, edited by G. Oertel, pages 267 *et seq.* (Verlag Carl Hanser, Munich 1993).

Rigid foams of this type are customarily produced by reacting aromatic polyisocyanates with relatively high molecular weight polyols, preferably polyether or polyester polyols in the presence of blowing agents, catalysts, flame retardants and other auxiliary substances and additives. It is also known that, instead of polyether or polyester polyols, it is possible to use mixtures of these stated structural components. One of the reasons for using such mixtures was the reduction in costs achieved by mixing costly polyester polyols suitable for the production of high quality rigid polyurethane (PU) foams with inexpensive polyether polyols. Suitable low-viscosity polyester polyols for the production of rigid PU foams having good mechanical properties are described, for example, in German Auslegeschrift 2,704,196.

All the stated processes rely on the use of CFC blowing agents to ensure that the desirable properties of rigid foams, including, for example, toughness, adhesion to surface layers and reduced flammability, are obtained.

According to German Offenlegungschrift 3,910,100, the use of CFC blowing agents is not necessary if the polyol mixtures claimed therein are used. A common feature of the stated processes is the use of conventional polyol systems based on petrochemicals. In order to reduce such dependency, the use of special natural products has attracted increasing technical interest in polyurethane chemistry. This particularly applies to the renewable raw material, castor oil, the use of which in rigid foam formulations is highly desirable on the basis of cost alone. There has thus been no lack of attempts to make use of castor oil in the polyol component.

U.S. Patent 2,955,091 describes elastic foams, wherein the polyol component consists of a mixture of conventional polyols and castor oil.

Rigid foams using castor oil are described in *J. Cell. Plast* 5, 364 (1969). Apart from the stated necessity of using CFC blowing agents, it is only by the use of special castor oil/polyol blends that it is possible to produce rigid foams with good dimensional stability which meet practical requirements.

The object of the present invention was thus to provide a novel process for the production of corresponding polyurethane rigid foams with elevated toughness, excellent adhesion and reduced flammability. This process

a) may operate with modified castor oil, and

b) avoids the use of CFC blowing agents.

As has surprisingly been found, this object could be achieved with the process according to the invention described below.

DESCRIPTION OF THE INVENTION

The present invention is directed to a process for the production of substantially closed-cell rigid foams containing urethane, urea and biuret groups. These foams have excellent adhesion to solid surfaces. This process comprises reacting

a) one of more organic polyisocyanates

with

b) modified castor oil

in the presence of

c) catalysts

and

d) water as blowing agent

wherein the modified castor oil has an OH number of 200 to 500, preferably 350 to 480, and is prepared by reacting castor oil with an amine, hydroxy compounds, or mixtures thereof.

In the present invention, it is also possible to use low-boiling hydrocarbons as an additional blowing agent in conjunction with water. It is also possible that the reaction of the isocyanate with the modified castor oil proceed in the presence of

e) auxiliary substances and/or additives known in the art of polyurethane chemistry.

Preferred embodiments of the present invention include the process wherein: 1) the reaction is performed at isocyanate indices of 100 to 130; 2) the amines used to prepare the modified castor oil are selected from the group consisting of alkanolamines, polyalkyleneamines, and mixtures thereof; and/or 3) the substantially closed-cell rigid foams containing urethane, urea and biuret groups have bulk densities of 20 to 200 kg/m^3.

The present invention also relates to insulating materials and/or mechanical structural components made from these substantially closed-cell rigid foams containing urethane, urea and biuret groups and having excellent adhesion to solid surfaces.

An essential feature of the invention is the use of the stated specially modified castor oils.

The suitable starting materials for this process include those aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates, such as those, for example, described by W. Siefken in *Justus Liebigs Annalen der*

Chemie, 362, pages 75 to 136. These include those polyisocyanates corresponding to, for example, the formula:

$$Q(NCO)_n$$

wherein:

n represents an integer from 2 to 5, preferably 2 to 3,

and

Q represents an aliphatic hydrocarbon residue having 2 to 18, preferably 6 to 10, carbon atoms; a cycloaliphatic hydrocarbon residue having 4 to 15, preferably 5 to 10, carbon atoms; an aromatic hydrocarbon residue having 6 to 15, preferably 6 to 13, carbon atoms.

Suitable examples of these polyisocyanates include those described on pages 10 to 11 of German Offenlegungschrift 2,832,253.

In general, it is particularly preferred to use commercially readily obtainable polyisocyanates such as, for example, 2,4- and 2,6-tolylene diisocyanate and any desired mixtures of these isomers ("TDI"), and polyphenylpolymethylene polyisocyanates, as are produced by aniline-formaldehyde condensation and subsequent phosgenation ("crude MDI"), and polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates"), and, in particular, those modified polyisocyanates derived from 2,4- and/or 2,6-tolylene diisocyanate, or from 4,4'- and/or 2,4'-diphenylmethane diisocyanate.

Suitable starting components for b) the modified castor oil include the reaction products formed by reacting castor oil with one or more amines, glycerol, or mixtures thereof. The OH number of these reaction products is about 200 to 500, preferably 350 to 480.

The amines suitable for the present invention include, preferably, products of the ethyleneamine series, such as, for example, tetraethylenepentamine, triethylenetetramine or diethylenetriamine. Amines of the alkanolamine type are also preferably used. These include compounds, such as, for example, mono-, di- or triethanolamine. The reaction of castor oil with one or more suitable amines proceeds, for example, by mixing the compounds at 40 to 250°C, preferably 50 to 180°C. Depending upon the selected temperature, the reaction times vary from about 1 to 24 hours, and preferably 2 to 16 hours.

It is also possible that castor oil may be reacted with a combination of one or more suitable amine and hydroxy compounds to yield a suitable reaction product for the present invention. Reaction times and temperatures generally fall within the scope of those set forth above with respect to the reaction of castor oil and one or more amine.

Suitable hydroxy compounds are those containing 2 to 6 hydroxyl groups and having OH numbers from about 1000 to about 1900, for example ethylene glycol, diethylene glycol, neopentyl glycol, glycerol, trimethylol propane, trimethylol ethane, pentaerythrite, sorbose.

Reaction products of castor oil and hydroxy compounds are produced by *per se* known oil transesterification (alcoholysis) at 100 to 250°C, preferably 150 to 200°C, wherein stirring is continued until the mixture is homogenized (from 2 hours to 30 minutes depending upon the selected temperature). In order to accelerate the reaction, catalytic quantities of basic metal compounds are added to the mixture. Suitable basic metal compounds include, for example, hydroxides, such as $Ca(OH)_2$, or alkoxides, such as $NaOCH_3$.

The quantities of castor oil, and amines and/or hydroxy compounds which are suitable for the present invention are determined by the OH number of the reaction product. Any quantities of these compounds may be used provided that the OH number varies from about 200 to 500, and preferably from 350 to 480.

Suitable catalysts for the present invention include those catalysts which are customary and known *per se* in polyurethane chemistry.

The blowing agent comprises water. Halogen-free blowing agents may also be used in conjunction with water. Some examples of suitable halogen-free blowing agents include compounds such as, for example, low-boiling alkanes such as pentane, cycloalkanes such as cyclopentane, alkenes, esters, ketones, ethers or the like.

These components, the modified castor oil, various polyurethane catalysts, water and other optional blowing agents, and any of the various optional additives, are reacted with the polyisocyanate a) in quantities such that the isocyanate index is between 90 and 150, preferably 100 to 130.

Suitable auxiliary substances and additives which are optionally used in the present invention include, for example, surface-active additives such as emulsifiers and foam stabilizers; and reaction retarders, cell regulators of the *per se* known type, such as, for example, paraffins or fatty alcohols or dimethyl polysiloxanes, together with pigments or dyes and flame retardants of the *per se* known type, such as, for example tris-chloroethyl phosphate, tris-chloropropyl phosphate, diphenylcresyl phosphate, tricresyl phosphate, together with stabilizers countering the effects of ageing and weathering, plasticizers and fungistatic and bacteriostatic agents, together with fillers such as barium sulfate, diatomaceous earth, carbon black or prepared chalk.

These optional auxiliary substances and additives are described in, for example, German Offenlegungschrift 2,732,292, pages 21-24.

Further examples of additives include surface-active additives and foam stabilizers together with cell regulators, reaction retarders, stabilizers, flame retardants, plasticizers, dyes and fillers, together with fungistatic and bacteriostatic agents which may optionally also be used according to the invention. Specific details relating to the use and mode of action of such additives may be found in, for example, *Kunststoff-Handbuch*, volume VII, edited by G. Oertel, Carl-Hanser Verlag, Munich, 1993, for example on pages 104-127.

The substantially closed-cell rigid foams containing urethane, urea and biuret groups and exhibiting excellent adhesion to solid surfaces are produced in a manner known *per se* to those in the field of polyurethane chemistry. The rigid foams produced according to the invention preferably have bulk densities of 20-200 kg/m^3.

The following examples further illustrate details for the process of this invention. This invention, which is set forth in the foregoing disclosure, is not to be limited either in spirit or scope by these examples. Those skilled in the art will readily understand that known variations of the conditions of the following procedures can be used. Unless otherwise noted, all temperatures are degrees Celsius and all parts are parts by weight.

EXAMPLES

Examples 1-6 are illustratative of the production of modified castor oil to be used according to the invention.

As used in examples 1-6, the term castor oil used refers to Brazil no. 1 castor oil, having an OH number of 160 (supplier for the castor oil used: Alberdingt Boley GmbH, Germany).

Example 1

930 g of castor oil and 184 g of glycerol are stirred together with 2 g of $Ca(OH)_2$ and stirred for 30 minutes at 200°C. A yellowish, homogenized mixture with an OH number of 433 is obtained.

Example 2

465 g of castor oil and 79 g of diethanolamine are stirred for four hours at 150°C. A yellow, clear liquid is obtained, having an OH number of 363.

Example 3

930 g of castor oil, 158 g of diethanolamine and 52 g of glycerol are stirred for four hours at 150°C. A yellow, clear liquid is produced, having an OH number of 433.

Example 4

465 g of castor oil, 47 g of tetramethylenepentamine and 55 g of glycerol are stirred for two hours at 150°C. A reddish, clear liquid is produced, having an OH number of 420.

Example 5

930 g of castor oil, 153 g of pentaethylenehexamine and 52 g of glycerol are stirred for 14 hours at 100°C. A reddish, clear liquid is formed, having an OH number of 405.

Example 6

930 g of castor oil and 261 g of triethanolamine are stirred for four hours at 150°C. A clear, reddish liquid if formed, having an OH number of 365.

Example 7

930 g castor oil, 335 g trimethylolpropane and 2 g $Ca(OH_2)$ are stirred for 30 minutes at 200°C. A clear, yellow liquid is obtained; OH-number: 447.

Example 8

1860 g castor oil, 73 g triethylenetetramine, 95 g tetraethylenepentamine and 469 g trimethylolpropane are stirred for 3 hours at 150°C. A clear, yellow liquid is obtained. OH-number: 435.

Example 9

1860 g castor oil, 636 diethyleneglycol and 4 g $Ca(OH)_2$ are stirred for 1 hour at 200°C. A clear, brown liquid is obtained; OH-number: 390.

Example 10

1860 g castor oil, 372 g ethyleneglycol and 4 g $Ca(OH)_2$ are stirred for 1 hour at 200°C. A clear, dark brown liquid is obtained; OH-number: 435.

Example 11

465 g castor oil, 91 g sorbose and 1 g $Ca(OH)_2$ are stirred for 2 hours at 200°C. A clear, yellow liquid is obtained; OH-number: 413.

Example 12

930 g castor oil, 224 g triethanoleamine and 52 g glycerol are stirred for 3 hours at 180°C. A clear, yellow liquid is obtained; OH-number: 430.

Example 13

930 g castor oil, 265 g diethyleneglycol, 61 g sorbose and 2,6 g $Ca(OH)_2$ are stirred for 60 minutes at 200°C. A clear, yellowish liquid is obtained; OH-number: 410.

Production of rigid foams
Foaming examples (quantities in parts by weight)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Catalyst 1	3.0	1.7	1.7	1.5	0.5	1.0	3.0	3.0
Catalyst 2	0.5	0.8	0.8	0.5	0.5	-	0.5	0.5
Stabilizer	1.3	2.0	2.0	1.3	1.3	1.3	1.3	1.3
Glycerol	-	-	-	3.7	-	-	-	-
Water	4.8	2.3	1.7	4.8	4.8	4.8	3.0	3.0
Cyclopentane	-	10.2	10.2	-	-	-	-	-
Flame retardant	10	-	-	-	-	-	10	-
Modified castor oil (Example 1)	81.6	-	-	-	40	-	82	82
Modified castor oil (Example 2)	-	-	-	78.3	-	-	-	-
Modified castor oil (Example 3)	-	98	102	-	-	-	-	
Modified castor oil (Example 4)		-	-	-	40	82	-	-
Isocyanate	174	150	146	174.6	174	174	131	131

Production of rigid foams
Foaming examples (quantities in parts by weight)

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8
Stirring time (s)	15	15	15	15	15	10	15	15
Latent time (s)	24	26	27	23	22	27	24	23
Gel time (s)	67	63	65	61	65	68	61	60
Surface	tough	tough	tough	tough	tough	tough	tough	tough
Interior	tough	tough	tough	tough	tough	tough	tough	tough
Cell size	1	1	1	1	1	1	1	1
Cell structure	1	1	1	1	1	1	1	1
Adhesion	good	good	good	good	good	good	good	good
Shrinkage RT*	none	none	none	none	none	none	none	none
Bulk density kg/m^3	29.4	26.6	30.4	21.8	31.6	29.8	44.4	43.2
Index	111	110	111	111	113	112	100	100

Cell size: 1-5; 1 = small cells, 5 = large cells   Cell structure: 1-5; 1 = good, 5 = poor
* RT = room temperature

Production of rigid foams
Foaming examples (quantities in parts by weight)

	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Catalyst 1	-	-	-	-	-	-
Catalyst 2	0.2	0.3	0.4	0.5	0.7	0.8
Stabilizer	1.5	1.5	1.5	1.5	1.5	1.5
Glycerol	-	-	-	-	-	-
Water	4.0	2.0	4.0	4.0	4.0	2.0
Cyclopentane	-	7.0	-	-	-	8.0
Flame retardant	10	-	10	10	10	10
Modified castor oil (Example 12)	85	85	-	-	-	-
Modified castor oil (Example 9)	-	-	85	-	-	-
Modified castor oil (Example 10)	-	-	-	85	-	-
Modified castor oil (Example 7)	-	-	-	-	85	85
Isocyanate	160	137	165	165	168	135

Production of rigid foams
Foaming examples (quantities in parts by weight)

	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14
Stirring time(s)	10	10	10	10	10	10
Latent time(s)	65	61	48	63	64	67
Gel time(s)	156	170	160	162	170	158
Surface	tough	tough	tough	tough	tough	tough
Interior	tough	tough	tough	tough	tough	tough
Cell size	1	1	1	1	1	2
Cell structure	1	1	1	1	1	1
Adhesion	good	good	good	good	good	good
Shrinkage RT*	none	none	none	none	none	none
Bulk density kg/m^3	35.6	40.2	38.8	38.1	38.1	34.2
Index	110	110	110	110	110	110

Cell size: 1-5; 1= small cells, 5 = large cells, Cell structure: 1-5; 1 = good, 5 = poor
* RT = room temperature

The following materials were used in Examples 1-14 in the tables.

Catalyst 1: Dimethylbenzylamine

Catalyst 2: Dimethylcyclohexylamine

Stabilizer: Tegostab B8421, a commercially available polyethersiloxane from Goldschmidt, Essen

Flame retardant: Diphenylcresyl phosphate

Isocyanate: Desmodur® 44V20, commercially available from Bayer AG

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A process for the production of substantially closed-cell rigid foams containing urethane, urea and biuret groups, comprising reacting

a) one or more organic polyisocyanates,

with

b) a modified castor oil having an OH number of 200 to 500, said modified castor oil being prepared by reacting castor oil with i) one or more amines, ii) hydroxy compounds, or iii) mixtures thereof,

in the presence of

c) one or more catalysts

and

d) a blowing agent comprising water.

2. The process of Claim 1, wherein said modified castor oil has an OH number of 350 to 480.

3. The process of Claim 1, wherein said blowing agent additionally comprises one or more low-boiling hydrocarbons.

4. The process of Claim 1, wherein said reaction of said polyisocyanate and said modified castor oil additionally occurs in the presence of

e) auxiliary substances and/or additives.

5. The process of Claim 1, wherein said reaction is performed at isocyanate indices of 100 to 130.

6. The process of Claim 1, wherein said amine is selected from the group consisting of alkanolamines, polyalkyleneamines, and mixtures thereof.

7. The process of Claim 1, wherein said hydroxy compounds contain 2 to 6 hydroxyl groups and OH-numbers of from 1000 to 1900.

8. The process of Claim 1, wherein said substantially closed-cell rigid foams containing urethane, urea and biuret groups have bulk densities of 20 to 200 kg/m^3.

9. Insulating materials and/or mechanical structure components made from the substantially closed-cell rigid foams obtainable from a process according to claims 1 to 7.